

Diffusive Exchange of Gaseous Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls Across the Air–Water Interface of the Chesapeake Bay

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Dissolved and gas-phase concentrations of nine polycyclic aromatic hydrocarbons and 46 polychlorinated biphenyl congeners were measured at eight sites on the Chesapeake Bay at four different times of the year to estimate net diffusive air–water gas exchange rates. Gaseous PAHs are absorbed into the bay's surface waters during the spring, and lighter compounds revolatilize in the late summer and early fall due to seasonal changes in surface water temperature and atmospheric PAH levels. On an annual basis, the atmosphere is a net source of volatile PAHs to the Chesapeake Bay, and gas absorption may be the largest external source of fluorene and phenanthrene, providing up to three times the combined loadings from wet and dry aerosol deposition and from tributaries. Largest PAH absorptive fluxes occurred in the northern Chesapeake when prevailing winds carried PAH-enriched air from the Baltimore-Washington urban area over the bay. In contrast to PAHs, PCBs volatilize from the Chesapeake Bay throughout the year, with the largest fluxes occurring in September and the smallest fluxes in June. However, higher chlorinated (6–8) homologues are absorbed by bay waters during most of the year. Highest PCB volatilization rates were observed in the northern Chesapeake Bay and near the James River in the southern bay, indicating volatilization offsets PCB loading from the bay's tributaries. Volatilization is the dominant removal process for PCBs from the Chesapeake Bay, removing an estimated 400 kg/year. This value is larger than current external PCB loadings, suggesting that release of PCBs from historically contaminated sediments supports volatilization from the bay.

Introduction

The Chesapeake Bay is a complex and fertile estuary that is of great importance for its living resources and for its

recreational value. Its highly dynamic geochemical cycles are driven by winter storms, tributary inputs, plankton blooms, summer stratification, fall water column turnover, and tidal mixing with the coastal ocean. The shallow (average depth is ~7.5 m), temperate (temperatures range from 1 to 30 °C) Chesapeake can be described as a thin veneer of water positioned between two large geochemical reservoirs (i.e., the atmosphere and the sediments) fed by large and highly variable riverine inputs. Exchange across the air–water and sediment–water interfaces likely controls concentrations and residence times of particle-reactive, semivolatile hydrophobic organic contaminants (HOCs) in this estuary, as has been shown in the Laurentian Great Lakes (1). During the past 5 years, initial estimates of annual loadings of HOCs such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to the Chesapeake have been made. Godfrey et al. (2) quantified HOC loadings from the Susquehanna and Potomac Rivers and have extrapolated these findings to estimate total riverine inputs of HOCs to the Chesapeake Bay. Leister and Baker (3) and Baker et al. (4) measured monthly and annual loadings of PAHs and PCB congeners to the bay via wet deposition and dry aerosol particle deposition. The strong influence of resuspension of sediments in driving temporal trends in water column contaminant inventories has been described (5, 6). Contaminant loadings inventories from urban sources to the Chesapeake Bay have also been estimated based on discharge permit data (7). Earlier studies have also catalogued contaminated sediment “hot spots” near Baltimore, Norfolk, and Washington (8, 9). While these initial HOC loading estimates have improved HOC mass balances for the Chesapeake Bay, to date, diffusive exchange of gaseous HOCs across the air–water interface is relatively poorly characterized. Recently, McConnell et al. (10) quantified gas exchange fluxes of chlorpyrifos and determined that this insecticide volatilizes from surface waters in the spring, but that gaseous chlorpyrifos deposits to the water column later in the year. Dickhut and Gustafson estimated PAH gas exchange rates at a single location in the southern Chesapeake Bay during Winter 1991 (11) and at several closely spaced sites along the western shore of the southern Chesapeake Bay in 1994 and 1995 (12). Several recent studies in the Great Lakes (13–19), Lake Baikal (20, 21), and the oceans (22) demonstrate the importance of exchange of gaseous HOCs as both a source to and sink from surface waters. The objectives of this study are to quantify temporal and spatial trends in the diffusive exchange of gaseous HOCs across the air–water interface of the Chesapeake Bay and to compare annual bay-wide gas exchange rates to other sources to determine the relative importance of air–water exchange as a source or sink of PAHs and PCBs in the Chesapeake Bay.

Experimental Section

Sampling. Surface water samples were collected at eight sites along a north to south transect of the mainstem Chesapeake Bay during four cruises in 1993 (Figure 1). Seven mainstem sites from Susquehanna Flats in the north to the Atlantic Ocean in the south were sampled to characterize open water HOC concentrations. An additional site near an area with PAH-contaminated sediments (8) in the mouth of the James River was also sampled. Cruises were conducted under widely varying meteorological and hydrodynamic conditions on 8–11 March (cold air and water, snowmelt, 4–6 °C), 12–14 April (maximum spring runoff, phytoplankton bloom, 8–13 °C), 1–4 June (warm surface waters, high primary production, low runoff, 17–21 °C), and 20–23

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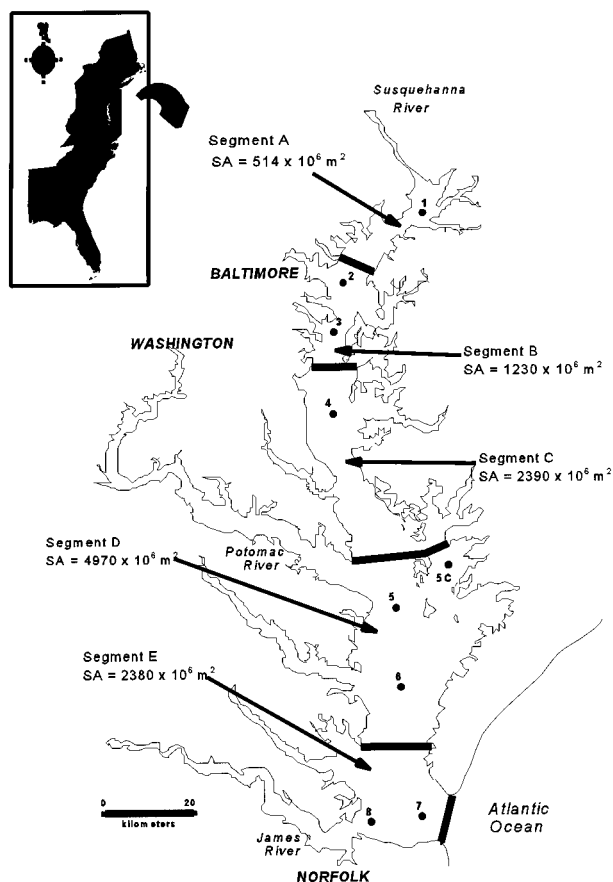


FIGURE 1. Sampling sites and area segmentation scheme used to calculate averaged gas exchange rates.

September (turnover, 21–25 °C). Paired air and surface water samples were collected to calculate instantaneous gas fluxes of the target HOCs.

Details of sampling and analytical methodologies are presented elsewhere (5, 23) and summarized here. Temperature, salinity, depth, and density were measured at each station (Seacat 19 profiler, Seabird Electronics), and wind speed and direction was estimated from recorded hourly wind velocities at the Baltimore-Washington International Airport (BWI), the Patuxent River Naval Air Station, and the Norfolk Naval Air Station. The hourly wind speeds from the closest monitoring site during the period of air sampling were averaged to calculate the wind speed for each water sample. These overland wind observations likely underestimate wind velocities over the water but provide accurate estimates of the wind direction.

Surface water samples were collected by pumping bulk water from two meters below the surface directly through a glass fiber filter (Schleicher & Schuell #25). Filtered water was collected in a polished stainless steel holding tank isolated from the ship's atmosphere and later pumped through a glass column packed with Amberlite XAD-2 resin which had been exhaustively cleaned and conditioned (5). The stainless steel tank was solvent rinsed after the water sample was processed to recover any analytes adsorbed to the walls. The resin samples were stored at 4 °C until analysis.

High volume air samples were collected 2.5 m above the water from the bow of the University of Maryland's *R. V. Aquarius* with a modified high volume air sampler (Model NY1123; General Metal Works; ref 3). Air samples were collected while the ship was underway on transects between sampling stations. Two cylindrical 8.5 × 10 cm polyurethane foam plugs (PUF) in series downstream of a glass fiber filter

captured gaseous HOCs. A flow rate of ~0.5 m³/min for 7–19 h sampling periods resulted in sample volumes of 273–660 m³. PUF samples were stored at –20 °C until analysis. Front and back PUF plugs were analyzed separately, breakthrough of gaseous HOCs to the second PUF plug was usually negligible, and gas-phase concentrations were calculated from the analyte collected in both PUF plugs.

Analysis. Samples were analyzed for PAHs and PCB congeners using methods described in detail elsewhere (3, 5, 23). Dissolved HOC (XAD-2 resin) samples were Soxhlet extracted with a 1:1 mixture (v/v) of acetone and hexane, partitioned against water to remove polar impurities, concentrated, and stored at –20 °C until analysis by gas chromatography/mass spectrometry (GC/MS). Gas-phase (PUF) samples were extracted in Soxhlet extractors with petroleum ethers, concentrated, solvent exchanged to hexane, and stored at –20 °C until analysis. After analysis of the concentrated extracts for PAHs by GC/MS, polar interferences were removed by eluting the extracts through a Florisil column (24) and the purified extracts were concentrated and analyzed for PCB congeners by gas chromatography using an electron capture detector (GC/ECD).

Each sample was analyzed for nine PAHs and 46 PCB congeners (26 individual congeners and 20 chromatographically unresolved congener groups). PAHs were identified and quantified using capillary gas chromatography (Hewlett-Packard 5890) with an electron impact mass spectrometer detector (5970A) operated in selective ion monitoring mode using at least one secondary conformation ion for each compound (3). PAHs were identified by retention time relative to a mixed standard (Ultra Scientific) and confirmed by the relative abundance of a secondary mass fragment compared to the molecular ion.

PCB congeners were analyzed using a Hewlett-Packard 5890 gas chromatograph with a 5% diphenyl-dimethylpolysiloxane capillary column and a ⁶³Ni electron capture detector. Each PCB congener was identified based on its retention time (±0.03 min) relative to a standard 25:18:18 mixture of Aroclors 1232, 1248, and 1262 (Ultra Scientific), whose peaks were identified based on the relative retention times of Mullin et al. (25). Internal standards added to calibration standards and samples prior to instrumental analysis were *d*₈-naphthalene, *d*₁₀-phenanthrene, *d*₁₂-benzo[*a*]anthracene, *d*₁₂-benzo[*a*]pyrene, and *d*₁₂-benzo[*ghi*]perylene for PAHs, and 2,3,6-trichlorobiphenyl (IUPAC 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (IUPAC 204) for PCBs.

Quality Control. Two perdeuterated PAHs (*d*₁₀-anthracene and *d*₁₂-chrysene) and one PCB not found in industrial synthesis (3,5-dichlorobiphenyl, IUPAC no. 14) were added to each water sample prior to extraction as surrogates to quantify overall procedural recovery. Recoveries of perdeuterated anthracene, chrysene, and PCB 14 from dissolved phase samples averaged 79 ± 20% (*n* = 53), 70 ± 15%, and 71 ± 17% (*n* = 53), respectively. Recoveries were low but consistent for the two surrogates added to the gas-phase samples (36 ± 21% of *d*₁₀-anthracene and 35 ± 20% of *d*₁₀-pyrene, *N* = 20). A PCB surrogate was not added to the gas-phase samples and gaseous PCB recoveries were estimated using *d*₁₀-anthracene, based on a strong correlation between PCB 14 and *d*₁₀-anthracene recoveries in other samples. These low recoveries were later traced to incomplete extraction. Fortunately, additional air samples were collected at three shore-based sites along the Chesapeake Bay from 1990 to 1993 (4). Surrogate-corrected gas-phase PAH and PCB concentrations from shipboard samples agree well with those shore-based measurements. For example, PAHs and PCBs concentrations in March compare well (±10%) to values measured during concurrent sampling at a nearby shore-based site (4), indicating that despite the

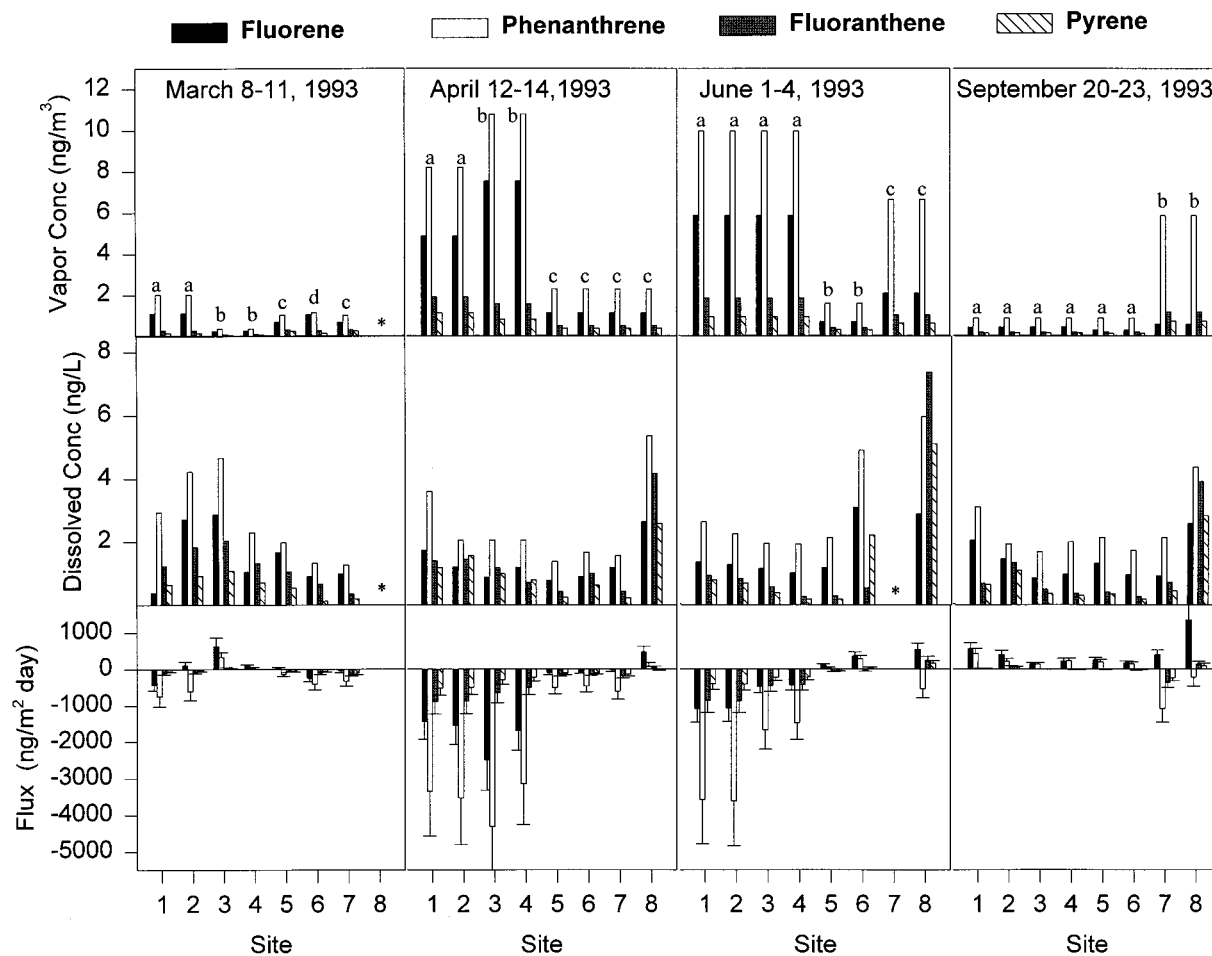


FIGURE 2. Gaseous and dissolved concentrations and instantaneous gas exchange fluxes of fluorene, phenanthrene, fluoranthene, and pyrene in the Chesapeake Bay, 1993. Each gas-phase concentration measured along transects among stations was used to calculate fluxes at one or more sites, as indicated by letters in the top panels. Negative fluxes denote gas absorption into surface waters. (*) No data available.

surrogate losses these samples represent viable gas-phase samples. Concentrations of all samples were corrected for the corresponding surrogate recoveries.

Laboratory blanks and field blanks were analyzed to quantify possible contamination of the samples during collection, transport, storage, and extraction. XAD resin field blanks contained levels of analytes roughly equivalent to those in the laboratory matrix blanks, and an overall average of all field and laboratory XAD resin blank was calculated. However, PUF field blanks contained higher levels of analytes than the corresponding laboratory blanks, indicating minor contamination in the field, and only the PUF field blanks were used to calculate method detection limits. Method detection limits were calculated as three times the mean matrix blank concentration for each HOC (3). Detection limits for PAHs in gaseous and dissolved samples ranged from 0.0007 ng/m³ (chrysene) to 0.033 (phenanthrene) ng/m³ and 0.0031 ng/L (benz[a]anthracene) to 0.010 (fluorene) ng/L, respectively. Gaseous and dissolved PCB congener detection limits ranged from 0.005 (congener 205) to 3.7 pg/m³ (congener 201), and 0.05 pg/L (congener 207) to 24 pg/L (congener 3), respectively. Many higher molecular weight PAHs and PCBs were below the detection limits in the dissolved and gas phases, and gas exchange fluxes could not be calculated for these relatively nonvolatile compounds.

Results and Discussion

Gas-Phase Concentrations. Gas-phase PAH concentrations were generally higher in the northern bay than in the southern

bay, with air collected near the southern bay sites 5 and 6 having consistently lower gas-phase PAH concentrations (Figure 2). The highest gas-phase PAH concentrations were measured during the April and June cruises. Gas-phase PAH concentrations in the northern bay were highly variable (0.36–10.8 ng/m³ phenanthrene and 0.07–1.90 ng/m³ fluoranthene, Figure 2), with higher concentrations measured when westerly winds blew from over the Baltimore-Washington metropolitan area. PAH gas-phase concentrations from this work are similar ($\pm 20\%$) to those measured at three shoreline sites in 1990–93 during the Chesapeake Bay Atmospheric Deposition Study (CBADS; ref 4).

Gas-phase PCB concentrations over the Chesapeake Bay were higher in June and September than in March. In contrast to PAHs, total PCB (sum of measured congeners; *t*-PCB) gas-phase concentrations were consistently lower in the northern bay (0.41 ± 0.28 ng/m³, range 0.20–0.92 ng/m³) relative to the southern bay (0.75 ± 0.41 ng/m³, range 0.33–1.43 ng/m³), and concentrations were consistently highest at site 8 near Norfolk, ranging from 0.34 to 1.57 ng/m³. Trichlorobiphenyls dominated the gas-phase homologue distribution except in April, when there were relatively more tetra chlorinated homologues (Figure 3). Air samples enriched in gaseous PAHs collected during westerly winds did not contain elevated levels of *t*-PCBs, suggesting that Baltimore-Washington air is enriched in PAHs relative to *t*-PCBs. The maximum and average gas phase *t*-PCB concentrations measured in this study (1.57 and 0.59 ng/m³, respectively) are higher than those measured earlier for

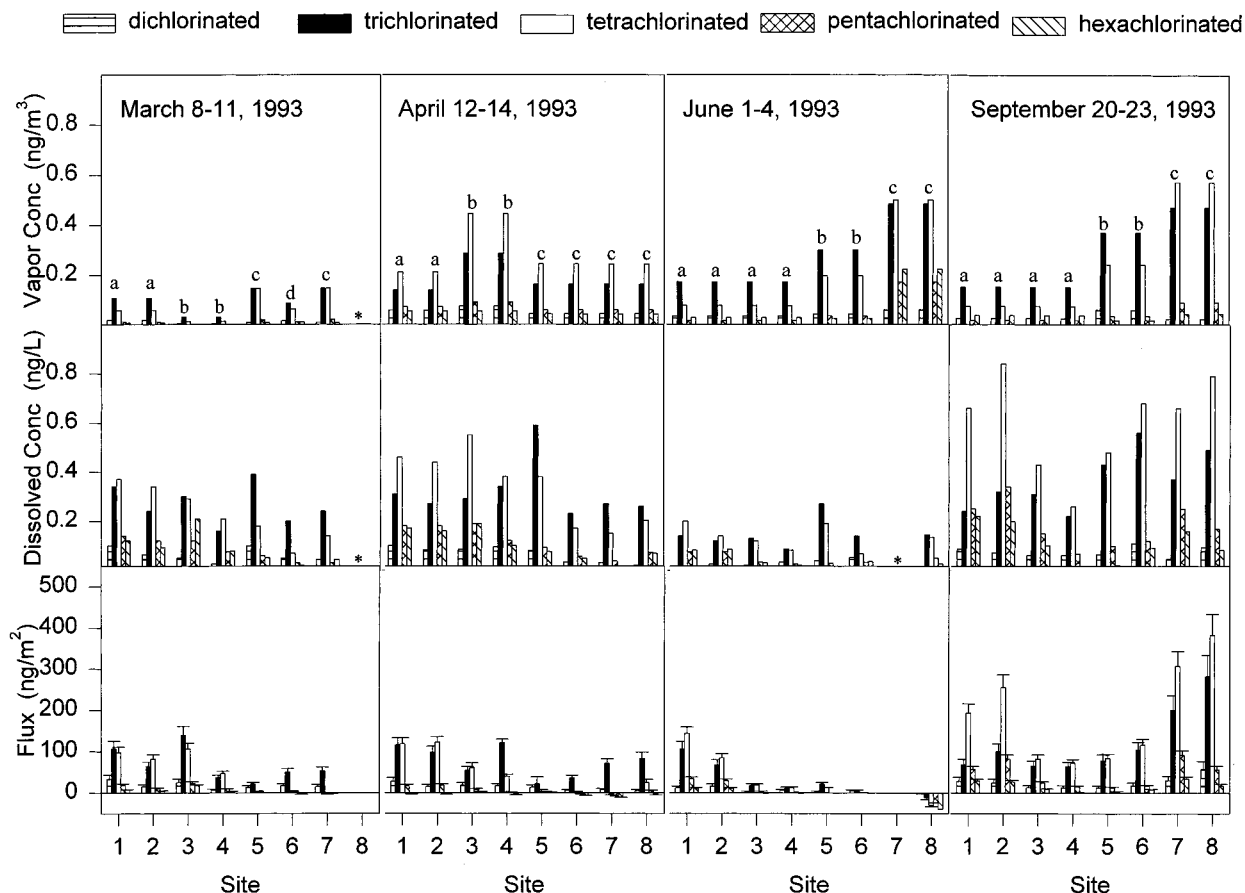


FIGURE 3. Gaseous and dissolved concentrations and instantaneous gas exchange fluxes of PCB homologues in the Chesapeake Bay, 1993. Individual congener concentrations were used to calculate compound-specific fluxes, which were then summed to calculate total homologue fluxes. Each gas-phase concentration measured along transects among stations was used to calculate fluxes at one or more sites, as indicated by letters in the top panels. Negative fluxes denote gas absorption into surface waters. (*) no data available.

CBADS (average *t*-PCB 0.31 ng/m³; ref 4), perhaps reflecting either a more frequent urban influence in the present study or consistently higher overwater PCB concentrations, as was observed in a comparison of over-water versus shoreline *t*-PCB concentrations in air over the Great Lakes (26).

Dissolved Phase Concentrations. Spatial and temporal trends in dissolved PAH and PCB concentrations in the Chesapeake Bay are discussed in detail elsewhere (23) and summarized here. Dissolved phase concentrations of fluorene, phenanthrene, fluoranthene, and pyrene averaged over the entire Chesapeake Bay during the four cruises in 1993 were 1.3, 2.4, 0.9, and 0.7 ng/L, respectively. Average dissolved phase PAH concentrations in the northern Chesapeake Bay above the Potomac River mouth (1.4, 2.6, 1.3, and 0.8 ng/L for fluorene, phenanthrene, fluoranthene, and pyrene, respectively) were similar to concentrations in the south bay region (1.2, 2.0, 0.5, and 0.5 ng/L for fluorene, phenanthrene, fluoranthene, and pyrene, respectively), with the noted exception of site 8. Site 8 consistently had the highest dissolved PAH concentration observed in this study by at least 50% (2.7, 5.2, 5.1, and 3.5 ng/L average for fluorene, phenanthrene, fluoranthene, and pyrene, respectively), likely due to its proximity to contaminated sediments (8, 27). Dissolved phase PAH concentrations did not vary systematically with season. Average dissolved PAH concentrations in the mesohaline bay, measured in 1993, are similar to those measured between 1990 and 1992 at a nearby location (5).

Dissolved *t*-PCB concentrations averaged 0.92 ± 0.47 ng/L ($N = 31$) over the entire Chesapeake Bay during the four cruises in 1993. Tri-, tetra-, and pentachlorobiphenyl congeners made up 30%, 35%, and 12% of the total dissolved

PCB concentrations, respectively. Dissolved *t*-PCB concentrations were higher in the northern bay than in the southern bay during the March and April cruises, but did not vary spatially when averaged over the four cruises. Unlike PAHs, dissolved *t*-PCBs concentrations were not elevated at site 8 with respect to other sites. The highest dissolved *t*-PCB concentrations measured throughout the bay in September (average of 1.4 ng/L) may be the result of the water column turnover. In contrast, the lowest dissolved *t*-PCB concentrations were measured in June (<0.6 ng/L) when the water column was highly stratified. Dissolved *t*-PCB concentrations measured in the mesohaline reaches of the bay in 1993 (0.66 ng/L average at site 4) agree well with those measured in the same area in 1990–1992 (0.6 ng/L; ref 5).

Calculation of Gas Exchange Rates. Instantaneous gas exchange rates were calculated for each analyte detected in both gas and dissolved samples at each location during each cruise. Details of these calculations, including Henry's Law constant (H) temperature corrections and calculating compound-specific mass transfer coefficients are detailed in the Supporting Information. The application of two film transport models to calculate fluxes of semivolatile organic contaminants has recently been reviewed (28, 29). Staudiger and Roberts (30) have compiled H values for organic chemicals and discussed variations with temperature and ionic strength. Instantaneous gas exchange rates across the air–water interface were modeled using the paired dissolved and gas-phase PAH and PCB congener measurements, temperature-corrected H values (31, 32), and estimates of mass transfer coefficients (K_{OL} s) based on correlations with wind speed. To be consistent with recently reported PCB

gas exchange rates in Green Bay (33) and Lake Michigan (13), we adopted the approach of those studies to estimate mass transfer coefficients and temperature-corrected H values (see refs 13, 23, and 33 and Supporting Information for complete details of these calculations). Henry's Law constants of semivolatile organic contaminants are very sensitive to temperature, with H increasing approximately 10-fold with a 25 °C increase in temperature (34). We used the equation proposed by Tataya et al. (34) to estimate temperature-corrected H values for both PCBs and PAHs:

$$\ln H_T = \ln H_{298} + 26.39 - \frac{7868}{T} \quad (1)$$

where H_T and H_{298} are the Henry's Law constants at temperature T and 298 K, respectively. The gas exchange mass transfer coefficient was estimated from correlations with wind speed (as a surrogate measure of surface turbulence) and molecular diffusivity in air and water, as described in Hornbuckle et al. (13, 14) and detailed in Nelson (23).

Error Analysis. Uncertainty in calculated instantaneous gas exchange fluxes result from systematic and random measurement errors, systematic errors in the values of H , and uncertainties due to the mass transfer coefficient calculations. To assess the relative magnitude of random errors in the instantaneous gas exchange flux calculations, propagation of error analysis (35) was performed:

$$\sigma^2(F) = \left(\frac{\partial F}{\partial K_{OL}}\right)^2 (\sigma K_{OL})^2 + \left(\frac{\partial F}{\partial C_d}\right)^2 (\sigma C_d)^2 + \left(\frac{\partial F}{\partial C_a}\right)^2 (\sigma C_a)^2 + \left(\frac{\partial F}{\partial H}\right)^2 (\sigma H)^2 \quad (2)$$

where F is the instantaneous gas exchange flux resulting from the difference in dissolved (C_d) and gas-phase (C_a) concentrations, accounting for H . Total propagated variance [$\sigma^2(F)$] is the linear combination of the weighted contribution of the variances (σ^2) of the mass transfer coefficient, H , and measured concentrations. The σH term is assumed equal to zero because H is a constant and under any singular condition there is no random error (deviations in estimated H values from their true values are systematic, not random errors). To estimate the overall random error in the flux calculation, measurement precision was estimated to be 10%, based upon repeated sample injections. While the total analytical uncertainty is likely greater than 10%, the overall propagated error in the flux is relatively insensitive to the error in the concentration term (see below). Uncertainty in K_{OL} was determined by propagating random errors in the air- and water-side transfer velocities (k_a and k_w), which here we assume to be 40% based on inspection of k_w versus wind speed plots in Wanninkhof et al. (36). Using these estimated errors, we calculate the overall random error of a typical instantaneous gas exchange flux as ~40%, with a majority of the uncertainty arising from K_{OL} . As a specific example, the flux of fluorene into site 1 on 8 March 1993 is 413 ± 139 ng/m² day, with 88% of the random error due to uncertainty in K_{OL} , and 11% and <1% of the error due to uncertainty in the measured gas-phase and dissolved concentrations, respectively. Propagation of error demonstrates that the significant improvements in estimating gas exchange fluxes will require better understanding of the mass transfer process itself rather than improved characterization of the concentration gradients. These estimates of propagated error are less than those calculated by Hoff (37) for atmospheric loadings to the Great Lakes because his calculations included systematic errors, the largest arising from uncertainty in H .

Significant sources of possible systematic errors include improper quantification of the concentration gradient due to including colloiddally bound contaminants in the dissolved

phase measurement (15, 38), underestimations of the wind effects on K_{OL} (36, 39), and using inaccurate values of H . Recent work by Alaee et al. (40) suggests that H for lighter weight PAHs may vary less with temperature than predicted by eq 1. If so, the fluorene and phenanthrene absorptive fluxes calculated during colder periods (March and April) using eq 1 may be overestimated. Henry's Law constants of organic compounds increase with salinity due to an increase in the aqueous activity coefficient. On the basis of their review of studies that compared H values measured in freshwater and seawater, Staudinger and Roberts (30) concluded that these constants increase at most 6-fold (41), but more commonly 2–4-fold in seawater, with the effect of salinity more pronounced for larger molecules. The salinity of the Chesapeake Bay surface waters ranged from 0‰ in the north to 27‰ in the south during this study, suggesting that H values may have increased 2–3-fold from north to south. Due to the lack of compound-specific H -salinity relationships, we could not make this correction in our calculation. The gas exchange fluxes in the southern bay may be biased, therefore, toward absorption.

Instantaneous Gas Exchange Rates: PAHs. PAH K_{OL} s ranged from 0.001 m/day for chrysene in March to 0.68 m/day for fluorene in September (see Supporting Information). The largest K_{OL} values were calculated in June and September when winds were greater than 5 m/s. Overall, K_{OL} was fairly constant during the four cruises as the balance between cold water with high wind velocity in March and April, and warm water with low wind velocity in June results in relatively invariant K_{OL} values during different times of year. K_{OL} did not vary spatially, as the surface water temperature and winds did not systematically change with location.

PAH fluxes varied both temporally and spatially in the Chesapeake Bay (Figure 2). Fluxes were usually larger in the northern bay (up to 7-fold in April), as a result of higher gaseous concentrations. Fluorene volatilizes from the southern bay, but this loss is less than the net absorptive deposition to the northern bay. Due to high dissolved concentrations, fluoranthene and pyrene volatilized from the northern bay in September, when easterly winds off the Atlantic Ocean resulted in relatively low gaseous concentrations. Elevated dissolved phase concentrations of all PAHs at site 8 resulted in volatilization when the wind was from the east. Gas exchange fluxes of the more volatile PAHs fluorene and phenanthrene were relatively large and variable, while fluxes of heavier PAHs were small as a result of either concentration gradients being close to equilibrium (benz[a]anthracene) or low K_{OL} (chrysene). Spatial and temporal trends in fluxes of methylated phenanthrenes were similar to those of phenanthrene.

Generally, gaseous PAHs absorb from the atmosphere into cold surface waters throughout most of the bay during March and April, and revolatilize during June in the southern bay and bay-wide in September. The largest net PAH gas absorption fluxes occurred in the northern bay during April (maximum of 4.3 and 0.9 µg/m² day for phenanthrene and fluoranthene, respectively), but large fluxes also occurred in June at these sites due to high gaseous concentrations. High net gas-phase absorption fluxes resulted from elevated gas-phase concentrations, cold surface waters, and high winds. During September, net volatilization of fluorene and phenanthrene from the bay occurred due to relatively low gas-phase concentrations and warm surface waters. PAH fluxes determined at site 6 are generally lower than those previously reported at a nearby location (11, 12; Table 1), but the estimates of fluoranthene diffusive exchange agree between the two studies. The larger fluxes in the earlier work result from higher dissolved PAH concentrations (42).

PCBs. PCB fluxes were calculated for individual congener or chromatographically unresolved congener pairs using

TABLE 1. Gas Exchange of PCBs and PAHs from Surface Waters

area	flux (ng/m ² day) ^a	period	ref
PCBs			
Lake Superior	+19 to +141	August	15
1986	+63	annual	1
1992	+13	annual	1
	+8.3	annual	1
Lake Michigan	+8.5 to +22	annual	45
	+244	annual	43
N. Lake Michigan	+34 (+24 to +220)	annual	14
S. Lake Michigan	+6.4 (−32 to +59)	annual	19
Lake Ontario	+81	annual	44
Green Bay	+13 to +1300	June–Oct	33
	+111 Avg	June	33
Lake Baikal	+48	June	21
	+4.3 to +42	May	20
Open Ocean	−40	June–Aug	22
	+5	Nov–Mar	22
Chesapeake Bay	+96 (−63 to +800)	annual	this study
PAHs			
Southern Chesapeake Bay			
fluorene	−795 to +220	annual	12
phenanthrene	−4660 to −80	annual	12
fluoranthene	−690 to +820	annual	12
pyrene	−330 to +79	annual	12
Chesapeake Bay			
fluorene	−90 (−2500 to +1350)	annual	this study
phenanthrene	−686 (−4320 to +430)	annual	this study
fluoranthene	−162 (−890 to +240)	annual	this study
pyrene	−86 (−520 to +160)	annual	this study

^a Positive flux = net volatilization; negative flux = net absorption.

TABLE 2. Annual Organic Contaminant Loadings to and Losses from the Chesapeake Bay

	annual loadings (kg/year)			net gas deposition ^a (or volatilization)	
	Susquehanna River ^b	wet deposition ^c	dry aerosol deposition ^d	(μg/m ² year)	(kg/year)
fluorene	122	16	12	300–(167)	379
phenanthrene	450	63	92	70–719	2875
anthracene	NA	6	6	31–(3.6)	130
2-methylphenanthrene	NA	NA	NA	46–104	702
1-methylphenanthrene	NA	NA	NA	16–44	280
Fluoranthene	1130	70	120	157–(13)	679
pyrene	1030	75	109	76–(9.7)	361
benz[a]anthracene	376	9	34	0.1–(1.9)	(4.6)
chrysene	330	29	85	2.1–4.1	29
t-PCB	165	13	20	(31–112)	(403)

^a Net annual source to bay, numbers in parentheses denote net annual losses from bay. ^b Ref 2. ^c Ref 4. ^d Calculated from measured ambient aerosol particle contaminant concentrations and an annual average dry aerosol deposition velocity of 0.49 cm/s (3, 4).

individual concentrations and *H* values, then were summed by homologue group (Figure 3, Supporting Information). PCB *K*_{OL}s ranged from 0.02 m/day for octachloro homologues in March to 0.79 m/day for dichloro homologues in September coincident with high winds and warm water. PCB *K*_{OL}s had similar temporal and spatial trends as those of PAHs, with the highest *K*_{OL}s in June and September when the wind velocity was above 5 m/s. Like PAHs, PCB *K*_{OL} decreases with increasing molecular weight. However, PCB *K*_{OL} values are larger than PAH values for compounds of comparable molecular weight due to lower *H* values.

PCB fluxes varied spatially and temporally (Figure 3). PCB congener concentration gradients were largest in September due to high dissolved concentrations and warm water. Unlike PAHs, PCB concentration gradients were not larger at sites adjacent to urban areas. PCB volatilization losses were largest in the northern bay and near Norfolk (309 and 291 ng/m² day average *t*-PCB). The large fluxes in the northern bay were due to high dissolved concentrations and relatively low

gas-phase concentrations, accompanied by high winds. Largest *t*-PCB volatilization fluxes were from site 8 in September (802 ng/m² day), due to high dissolved concentrations coupled with high winds and high water temperature. PCB congeners generally volatilize from the Chesapeake Bay throughout the year, in contrast to gaseous PAHs, which deposit from the atmosphere to the bay.

Despite warm water temperatures, generally the lowest PCB fluxes occurred during stratification in June when both dissolved phase concentrations and wind speeds were low. In contrast, the largest PCB volatilization fluxes occurred in September when the water temperature and the dissolved concentrations were highest. PCB fluxes were also elevated in April (up to 272 ng/m² at site 1) as a result of higher wind speeds and a slightly enriched dissolved phase. Early spring storms and fall turnover resuspend surficial sediments as well as delivering heavy PCB loads from the major tributaries including the Susquehanna, James, and Potomac Rivers. At sites with elevated suspended solids concentrations in surface

waters (i.e., the northern bay and site 8), volatilization of tetrachlorinated biphenyls contributed 45% of the *t*-PCB flux. Trichlorinated congeners dominated at sites with lower suspended solids. Net fluxes of hexa, hepta, and octa chlorinated homologue groups were usually from air to water, and were small relative to those of the less chlorinated homologues.

The average *t*-PCB flux for the Chesapeake Bay was approximately 96 ng/m² day. This flux is lower than *t*-PCB average volatilization rates of 141 ng/m² day (winds of 5 m/s; ref 15), but higher than 63 ng/m² day estimated for Lake Superior (ref 1, Table 1) and 34 ng/m² day estimated for Lake Michigan (14). Instantaneous fluxes as high as 225 ng/m² day were reported by Hornbuckle et al. (14) for Lake Michigan and up to 1300 ng/m² day over Green Bay (33), whereas the highest value in this study was 802 ng/m² day. Calculations by Strachan and Eisenreich (43) estimate the *t*-PCB volatilization flux from Lake Michigan to be 240 ng/m² day, which is also greater than the Chesapeake Bay flux.

Relative Importance of Gas Exchange Fluxes in Chesapeake Bay Contaminant Budgets. Annual net gas exchange fluxes (μg/m² year) and loadings (kg/year) of PCBs and PAHs in each region of the bay (Figure 1) were calculated by first temporally interpolating among the four cruises, assuming that each sample represents a distinct water column period during the course of the year (first cruise, two months in late winter and early spring; second cruise, two months in spring; third cruise, three months in summer; and fourth cruise, one and one-half months of late summer/early fall). These interpolated fluxes and loadings (covering eight and one-half months) were then extrapolated to estimate annual average fluxes and loadings for each segment, and the loadings were totaled to calculate bay-wide annual loads (Table 2). All PAHs except benz[a]anthracene are absorbed from the air into surface waters on a net annual basis (Table 2). PCBs are volatilizing from the bay with an average annual flux of 35 μg/m² year. These gas exchange loadings are substantially higher than estimates of atmospheric wet and dry aerosol deposition to the bay (4), and thus gas exchange is the dominant mechanism of exchanging volatile PAHs and PCBs across the air–water interface of the Chesapeake Bay. Gas absorption contributes 93 and 95% of the total atmospheric loading of fluorene and phenanthrene, respectively, to the Chesapeake. Dry aerosol particle deposition and wet deposition become increasingly more important processes for the higher molecular weight PAHs as gas-phase concentrations decrease with increasing molecular weight. For example, gas exchange contributes only 20% of the chrysene load from the atmosphere. Annual *t*-PCB loss from the bay by net volatilization (400 kg/year) is more than 10 times larger than inputs to the bay from wet and dry aerosol deposition (37 kg/year, ref 4) and is more than twice the estimated *t*-PCB loading from the Susquehanna River (165 kg/year; ref 2), the estuary's largest tributary accounting for 60% of freshwater inputs. In addition, the annual *t*-PCB volatilization loss is nearly three times the estimated average PCB inventory in the Chesapeake Bay water column (23), suggesting very short (e.g., weeks to months) residence times and additional sources of PCBs to the bay's surface waters. Release of PCBs from contaminated surficial sediments during tidal and storm-induced resuspension events (5, 6) may replenish water column inventories and support the estimated PCB volatilization flux from the estuary. As is the case with the northern Great Lakes (1, 13, 14), the surface waters of the Chesapeake Bay are a net annual source of PCBs to the atmosphere, and volatilization might be the dominant process driving the long-term cleanup of PCBs from the bay.

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Supporting Information Available

Four tables (42 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$70.50 for photocopy (\$72.50 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL <http://www.chemcenter.org>. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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